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**NITRIC OXIDE, WATER VAPOR,
AND OZONE IN THE ATMOSPHERE
AS MEASURED IN SITU
FROM AN AIRCRAFT**

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NITRIC OXIDE, WATER VAPOR, AND OZONE IN THE ATMOSPHERE

AS MEASURED IN SITU FROM AN AIRCRAFT*

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SUMMARY

As part of the instrument evaluation plan for the NASA Global Atmospheric Sampling Program, prototype instruments were tested aboard the NASA Convair 990 during four flights in January and February of 1974. All the data were taken in maritime air between Hawaii and San Francisco and between Hawaii and 155° W, 35° N. A chemiluminescent instrument was used to measure nitric oxide. Readings ranged from ≤ 0.05 ppbv, the limit of detectability of the instrument, to 0.41 ppbv. Water vapor, which was measured by using an aluminum oxide hygrometer, ranged from 5.2 microgram per gram to saturation. Ozone was measured by an instrument using the ultraviolet absorption technique and ranged up to 235 ppbv. Typical temporal plots of the concentrations of the three constituents are presented. All the constituents showed considerable spatial and day-to-day variation in concentration at each altitude flown. Measurements of the three constituents were made simultaneously at various altitudes between 7.6 and 12.5 kilometers.

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INTRODUCTION

The NASA Global Atmospheric Sampling Program (GASP) is currently under way to equip several commercial Boeing 747 airliners with a system to obtain, routinely, in-situ measurements of several minor atmospheric constituents on a global basis. The system, as installed on the airliner, must be designed to operate unattended and may be inaccessible for periods ranging up to several weeks. The constraints as well as the aircraft environment impose severe demands on the instruments required to measure concentrations at altitude. Only proven atmospheric constituent measurement techniques are used in this program.

The need for obtaining reliable data on the concentrations of a number of minor atmospheric constituents arises from the continuing concern about the effects of aircraft engine exhaust emissions on the troposphere and stratosphere. Several exhaust constituents, including oxides of nitrogen, water vapor, and particulates, have been suggested to have potentially harmful effects (refs. 1 and 2). Furthermore, it is necessary to obtain information for both vertical and horizontal fluxes of these constituents in order to provide inputs for atmospheric models.

This report describes flight tests of prototype instruments for the GASP program. Three gas sampling instruments were included in the installation: (1) a chemiluminescent nitric oxide monitor, (2) an ultraviolet absorption ozone monitor, and (3) an aluminum oxide water-vapor hygrometer. All the data were taken in maritime air during January and February of 1974 between Hawaii and San Francisco and between Hawaii and 155° W, 35° N.

SAMPLING SYSTEM

A schematic of the sampling system for ozone and nitric oxide as installed in the Convair 990 is shown in figure 1. The stainless-steel inlet and discharge probes were mounted on a window blank and installed in the forward part of the aircraft. Isolation valves and a bypass line permitted purging of the assembly at altitudes below those where measurements were taken. The probe assembly penetrated the aircraft skin sufficiently to avoid ingestion of boundary-layer air.

The nitric oxide (NO) instrument operated at pressures near that governed by the aircraft altitude. A manual throttle valve immediately upstream was used to adjust the sample flow in flight. The instrument was connected to the inlet probe assembly by about 3.5 meters of 1.3-centimeter-outside-diameter tetrafluoroethylene (TFE) tubing, and the gas residence time in the tubing was not more than 0.4 second. No tests were made to check possible effects of the inlet system on the NO concentration.

For the ozone (O_3) instrument a dual-stage metal-diaphragm pump in combination with back-pressure regulator 1 was used to maintain the sample gas inlet pressure near 10.2 newtons per square centimeter. Any excess flow delivered by the pump was vented through the back-pressure regulator. The flow rate through the instrument was maintained constant by having a constant pressure differential across the instrument. The exhaust pressure was maintained at 8.2 newtons per square centimeter by a second regulator 2. This regulator used the reference pressure from an absolute pressure regulator 3 to establish the constant exhaust pressure. A manual throttle valve was used to set the instrument flow at 3000 cubic centimeters per minute. This flow system is described in more detail in reference 3. The advantages of operating the ozone instrument at higher than cabin pressure included a gain in instrument sensitivity and elimination of leaks into the ozone lines.

The ozone instrument was mounted as close as possible to the inlet assembly. All materials past the inlet probe valves were either made of TFE (tubing) or TFE coated. The gas residence time was kept as short as possible by mounting the instrument close to the inlet probe. Experiments conducted at the NASA Lewis Research Center indicated that the inlet tubing would remove less than 10 percent of the O_3 .

The aluminum oxide water-vapor (H_2O) sensor and thermistor were mounted in a commercial deiced total-temperature air scoop. The scoop was mounted on an aluminum plate which was substituted for one of the forward aircraft windows. The air within the scoop was changed in less than 0.1 second, so that the response time was short.

The pressurization system, the ozone and nitric oxide instrument, as well as the electronics for the water-vapor sensor were mounted on racks designed for use aboard the Convair 990 aircraft. Instrument outputs were monitored on strip-chart recorders.

GAS SAMPLING INSTRUMENTS

Nitric Oxide Monitor

The chemiluminescent NO instrument was similar to that described previously (refs. 4 and 5) but with several modifications necessary for adaptation to the Convair 990 aircraft. Ozone was produced by passing dried cabin air through a 400-hertz silent-discharge ozonizer contained in the instrument. The photomultiplier was cooled by a thermoelectric housing. Onboard calibrations were made when desired by adding small known flows of NO from a cylinder to the main airflow. Housekeeping signals, airflow, temperature, pressure, and calibration flows were multiplexed and recorded on a strip chart. A second strip chart recorded the output of the photon counting system.

The chemiluminescent intensity I is related to the total standard volume airflow F , mole fraction of NO X_{NO} , and pressure P by the relation

$$I = \frac{cFX_{\text{NO}}}{P}$$

where c is a proportionality constant. Thus, for maximum sensitivity, the instrument pressure should be low and the flow rate large. The total flow rate was limited to ≤ 300 cubic centimeters per second (at standard temperature and pressure) by the capability of the ozonizer. Pressures were determined by the aircraft altitude. The limit of detection of the instrument near 12.2 kilometers was about 0.5 ppbv or approximately 3×10^8 molecules per cubic centimeter. Since the chemiluminescence produced by the reaction of NO with O_3 is a broadband continuum, it cannot be distinguished from chemiluminescence produced by the reaction of O_3 with other gases. Although it is unlikely that other gases will be present to react with O_3 , strictly speaking, the measurements must be considered to provide only an upper limit to the NO concentrations.

Ozone Monitor

Ozone measurements were made with a self-contained ultraviolet absorption photometer (ref. 6). The operation of this instrument was based on the measurement of the absorption by ozone at 2537×10^{-10} meter (2537 \AA) in an absorption chamber 35.6 centimeters long. Measurements were updated after two half-cycle integration periods (every 20 sec). During the first half cycle, the sample air was scrubbed of ozone by being passed through a catalyst. This operation established a digital reference light measurement. During the second half cycle the ozone was not scrubbed, and the digital light intensity was integrated over the same time period as the reference measurement. The difference between the two measurements was related to the ozone concentration through Beer's law. Its accuracy had been verified to within ± 20 ppbv by using the standard potassium iodide method. Measurement precision of the instrument was ± 5 ppbv. The instrument could respond to a 90-percent step change in ozone concentration in approximately 30 seconds. Both zero and calibrated functions were provided on the instrument to check the electronic calibration.

Water-Vapor Monitor

The water-vapor monitor (refs. 7 and 8) consisted of two parts: a sensing element and an electronics package. The sensing element consisted of a small strip of aluminum which was anodized to provide a porous oxide layer. A very thin coating of gold was evaporated over this structure. The aluminum base and the gold layer formed the two electrodes of a capacitor. The impedance of this capacitor varied with the amount of water absorbed into the porous surface.

RESULTS

Measurements were made on four flights, two between Honolulu, 155° W, 20° N, and San Francisco, 123° W, 38° N, and two between Honolulu and 155° W, 35° N over the period January 30 to February 4, 1974. The NO, O₃, and H₂O mixing ratios in ppbv, and microgram per gram, respectively, are shown in figure 2. The circle near 155° W, 35° N encloses an area where the aircraft flew a specific pattern over an anchored ship as part of another mission.

In general, the water-vapor results did not show as large a variation with altitude or location as did the O₃ and NO data. The exception was the February 4th flight, where there was a significant increase at both 8.8 and 12.5 kilometers compared with other days. All the H₂O data presented in figure 2 are for conditions where no visible clouds were present in the flight path. The average H₂O volume mixing ratio between 7.6 and 12.5 kilometers for all flights was 10.4±3 microgram per gram. The accuracy of the values recorded was ±45 percent.

The observed NO volume mixing ratios had large uncertainties of about ±50 percent because of the low concentrations encountered compared with the sensitivity of the instrument at the operating pressure. However, some general observations can be made. First, the NO mixing ratios were quite low; they ranged from the limit of detection LD (~0.05 ppbv) to 0.4 ppbv. Second, there was considerable patchiness at a particular altitude on a given day, for example, the January 30th flight at 10.7 kilometers. Third, there was considerable variability from day to day at equivalent altitudes and locations; for example, in the 8.8- to 10.0-kilometer range between Honolulu and 155° W, 35° N on February 1st the NO levels were more than a factor of 2 higher than on February 3rd and 4th. Fourth, there was considerable variation at equivalent altitudes, for example, at 12.5 kilometers for February 4th and January 30th.

There may also have been a slight altitude trend to lower mixing ratios near 12.2 kilometers. Averaged results for all flights in the altitude ranges 12.2 to 12.5, 10.0 to 10.7, and 7.6 to 8.8 kilometers were 0.09±0.04, 0.12±0.06, and 0.13±0.07 ppbv, respectively. These averages were computed by using 0.05 ppbv as the limit of detection.

On January 30th, in the region between 135° W and 140° W at 10.7 kilometers, there was a "cloud" of higher NO compared with the rest of that flight leg. On February 4th at 12.5 kilometers there was again an increase in NO in the same location but at a much lower mixing ratio. This increase may have been caused by the vertical transport of NO from the lower stratosphere due to the passage of the aircraft through the jet stream at this location.

The O_3 data also showed considerable variability. However, there was no direct correlation between NO and O_3 within the accuracy of the data. As mentioned previously, the accuracy of the O_3 data was only ± 20 ppbv. The precision was, however, ± 5 ppbv, and relative comparisons should be meaningful. Patchiness was exhibited during the February 4th flight at 12.5 kilometers and on the January 30th flight at 10.7 kilometers. Day-to-day fluctuations were evident from a comparison of all flights at either 10.7 or 12.5 kilometers. Significantly lower values were observed on February 1st at 12.5 kilometers, and these did not change greatly down to 7.6 kilometers. Again large increases in O_3 might correlate with jet stream location where higher mixing ratios could be transported downward from the stratosphere on the cyclonic side of this jet.

CONCLUDING REMARKS

The test flights indicated the range and kind of variability that may be expected in routine tropospheric air sampling. They also demonstrated that the sensitivity of the nitric oxide instrument should be increased for evaluation of significant trends or correlations.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, October 22, 1974,
505-03.

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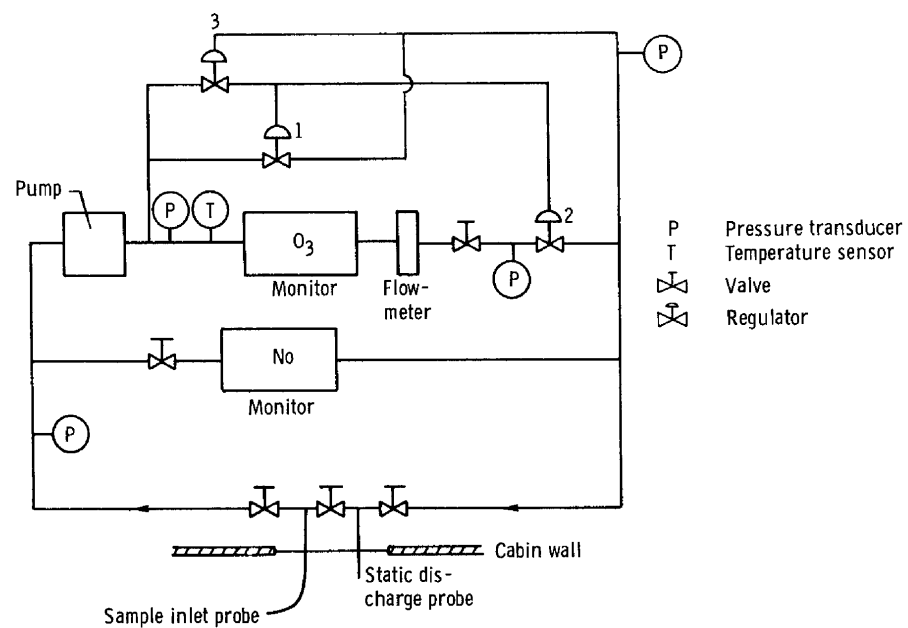
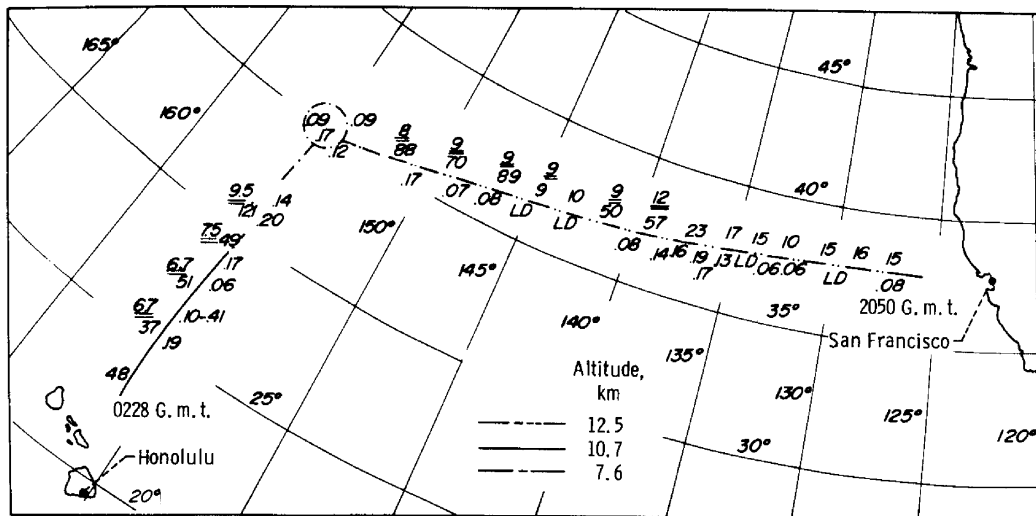
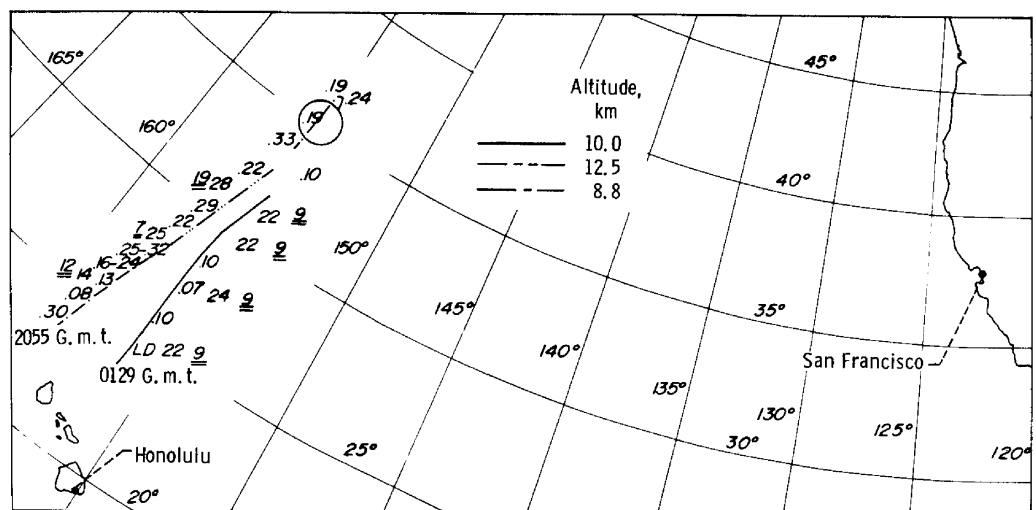


Figure 1. - Schematic of gas sampling system for nitric oxide and ozone instruments.

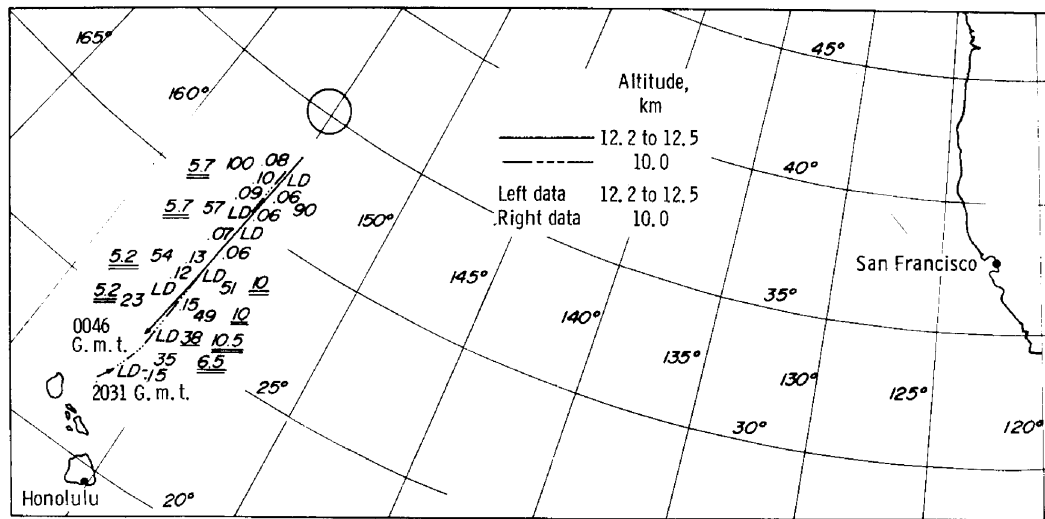


(a) January 30, 1974.

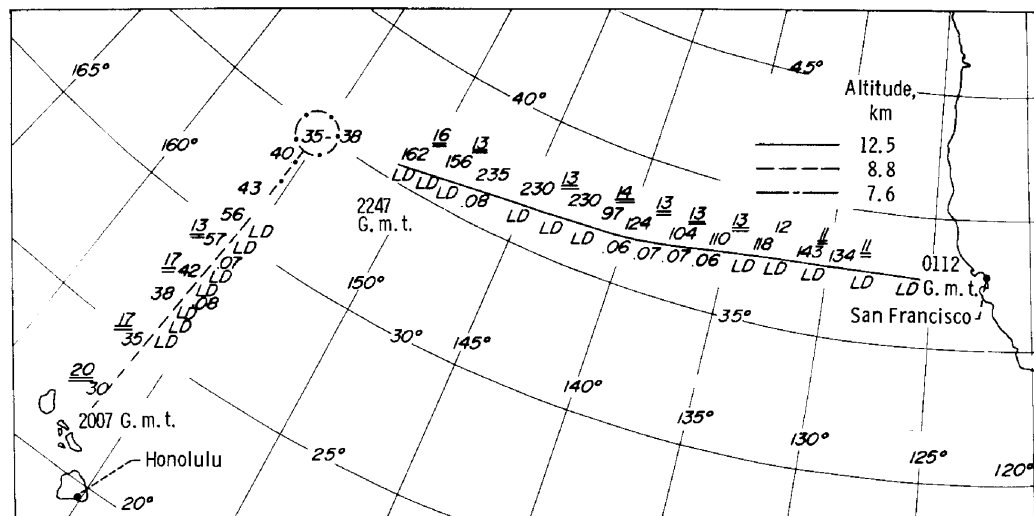


(b) February 1, 1974.

Figure 2. - Mixing ratios for nitric oxide (values not underlined, in ppbv), ozone (values with single underline, in ppbv), and water vapor (values with double underline, in $\mu\text{g/g}$). Limit of detection for nitric oxide LD, approximately 0.05 ppbv.



(c) February 3, 1974.



(d) February 4, 1974.

Figure 2. - Concluded.